

## Supplementary Information

# Discovery and characterization of a new family of lytic polysaccharide mono-oxygenases

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## Supplementary Results

**Supplementary Data Set** lists the more than 450 sequences that were retrieved with significant e-values using BAE61530 as the query for a BLAST search (23 Sep 2013) against the non-redundant protein sequence database of the NCBI.

		1		10		20		30																															
BAE61530	As_oryza	C	S	S	E	G	T	W	N	C	I	.	G	G	S	S	F	Q	R	C	A	N	G	Q	.	W	T	A	V	Q	Q	M	A	T	G	T	B	C	
EAA34256	Ne_crass	C	T	T	E	G	A	W	N	C	I	.	G	G	S	S	F	Q	R	C	A	S	G	A	.	W	S	A	V	T	Q	M	A	A	G	T	S	C	
CBF74037	As_nidul	C	T	D	E	G	S	W	N	C	I	.	G	G	S	S	F	Q	R	C	A	S	G	T	.	W	T	E	V	Q	T	L	S	S	G	T	B	C	
AEO61991	My_therm	C	T	E	E	G	A	W	N	C	I	.	G	G	T	Q	F	Q	R	C	A	S	G	V	.	W	S	A	P	Q	P	V	S	A	G	T	V	C	
AEO71776	Th_terre	C	S	N	E	G	Q	W	N	C	I	.	N	G	T	T	F	Q	R	C	A	S	G	V	.	W	S	A	V	Q	A	V	A	P	G	T	S	C	
CAP96550	Pe_chrys	C	S	T	E	G	Q	W	N	C	I	.	S	G	T	A	F	Q	R	C	A	S	G	T	.	W	S	V	A	Q	P	M	S	T	G	T	Q	C	
CAK40369	As_niger	C	S	V	E	G	E	W	N	C	I	.	N	G	S	S	F	Q	R	C	A	N	G	Q	.	W	T	P	A	Q	N	V	A	A	G	T	Q	C	
CAK38942	As_niger	C	S	Q	E	D	Y	W	Y	C	N	.	G	G	T	A	F	Q	R	C	V	N	G	E	.	W	D	A	S	Q	S	M	A	A	G	T	B	C	
BAE64395	As_oryza	C	S	E	E	G	A	W	Y	C	N	.	G	G	T	A	F	Q	R	C	V	N	G	Q	.	W	D	A	S	Q	N	M	A	D	G	T	A	C	
CAP70884	Po_anser	C	Q	N	E	G	S	W	N	C	L	.	.	G	D	G	F	Q	R	C	A	S	G	T	.	W	S	V	V	Q	A	M	A	S	G	T	K	C	
CCD52974	Bo_fucke	C	T	S	E	G	M	F	N	C	I	.	S	G	T	S	Y	Q	Q	C	G	S	G	T	.	W	S	V	V	M	Q	M	A	S	G	T	T	C	
EHA57166	Ma_oryza	C	T	D	E	G	A	Y	L	C	L	.	A	G	T	S	F	Q	R	C	A	S	G	S	.	W	S	S	P	I	P	M	A	P	G	T	S	C	
EHA51197	Ma_oryza	C	T	.	D	G	T	F	N	C	I	.	E	G	G	T	K	Y	Q	Q	C	A	H	G	K	.	W	Q	A	T	M	S	M	A	P	G	T	T	C
EHA52406	Ma_oryza	C	T	.	P	G	Q	F	K	C	V	.	G	G	S	A	F	Q	Q	T	A	G	Q	V	W	.	A	A	Q	I	Q	M	A	A	G	T	K	C	
CBX94475	Le_macul	C	T	T	N	G	A	I	I	C	N	.	G	T	T	K	F	G	L	C	N	A	G	K	.	.	V	V	W	Q	D	V	A	A	G	T	T	C	
AEO63862	Th_terre	C	S	P	N	G	A	L	I	C	F	.	S	P	T	T	F	G	L	C	A	N	G	F	.	.	A	I	P	Q	P	V	A	P	G	T	T	C	
AEO55680	My_therm	C	S	E	N	G	A	I	I	C	F	.	S	P	T	S	F	G	L	C	A	N	G	I	.	.	A	I	P	Q	P	V	A	A	G	T	T	C	
EHA52778	Ma_oryza	C	A	T	D	G	E	L	I	C	I	.	G	A	Q	Q	F	G	I	C	N	F	G	Y	.	.	A	L	P	Q	D	L	A	A	G	T	A	C	
CAK42338	As_niger	C	V	.	D	G	A	I	I	C	G	P	G	G	T	S	W	S	M	C	S	N	G	R	.	P	V	H	M	G	S	V	A	A	G	M	Y	C	
CBF89147	As_nidul	C	V	.	T	G	T	I	I	C	S	E	D	G	N	S	W	S	L	C	D	Q	G	F	.	P	V	H	M	G	S	V	A	P	G	T	R	C	
BAE59063	As_oryza	C	R	.	D	G	S	I	I	C	S	E	D	G	Q	T	W	S	M	C	T	F	G	H	.	P	T	F	M	G	P	V	A	A	G	M	R	C	
CAP96976	Pe_chrys	C	H	.	S	G	D	I	I	C	S	P	D	G	L	S	F	A	M	C	T	H	G	K	.	P	I	F	M	G	P	V	A	A	G	T	I	C	
JGI:439135	Le_palus	C	A	.	P	D	G	S	I	Q	C	N	.	G	E	S	A	F	S	M	C	V	Q	G	.	W	V	N	M	G	S	V	A	A	G	T	K	C	

Supplementary Figure 1. X278 alignment

		1	10	20	30	40
EHA51197	Ma_oryza	HM	MAM	KPF	PGT	ISSVQ
EHA52406	Ma_oryza	HM	LLAY	PPF	PGN	QNGPL
EHA52778	Ma_oryza	HM	IMNT	PV	YNLNGQ	APLLQTS
EAA35129	Ne_crass	HM	VMRT	PP	SYNLYKG	DTLLQV
AE063862	Th_terre	HM	IMNT	PT	PYNLRGT	SKLLQVN
AE055680	My_therm	HM	IMNT	PT	PYNLYHG	DNAVQVN
EHA52554	Ma_oryza	HM	ILQKBA	AAL	SYKGNPTLEK	DIDYSITS
AE063051	Th_terre	HM	EMTS	PP	PLKSKSNPH	TSPSNVDSMT
CAP96976	Pe_chrys	HM	QMSK	PP	PIRSPLNKEAK	GQKDYSTN
CAK42338	As_niger	HM	QMSN	PP	PIRSPLDPNG	DESCKDYSYN
BAE59063	As_oryza	HM	QMSK	PP	PIRSPLNKDAD	GKDYSTYN
CBF89147	As_nidul	HM	QMSK	PP	PIRSPLNQAT	GKDYSTYN
CCD54857	Bo_fucke	HM	SLTW	PL	PPRSKLNPN	SVSQSDYSIT
EHA57166	Ma_oryza	HM	EMTS	PP	PLRSKYNPAATT	KDSMDV
EAA34256	Ne_crass	HM	EMTS	PP	PPRSKKNPNAD	PKIDYSMT
AE061991	My_therm	HM	QVET	PP	PPRSKKNPNVD	SSMIDYSIT
CAP70884	Po_anser	HM	EISB	AP	PPRSKKNPHATN	IDYTN
AE071776	Th_terre	HM	EIQB	AP	PPRSKKNPN	AVNIDYTN
CBX94475	Le_macul	HM	KITD	PP	PPS	VATLDT
EAA28891	Ne_crass	HM	MTF	PI	PPYA	SPQGN
CBX92880	Le_macul	HM	IKB	PI	PPG	EQTKN
CCD52974	Bo_fucke	HM	IMTS	PI	PPYG	VDSLNS
CAP73493	Po_anser	HM	LLRT	PP	PPYT	SPALVQ
CBF74037	As_nidul	HM	VMTN	PP	PPYN	PKSWDN
CAP86617	Pe_chrys	HM	RMTS	PP	PPGSS	RKTLDN
CAP79267	Pe_chrys	HM	RMAS	PP	PPGSS	RKTLDN
CAP79288	Pe_chrys	HM	RMAS	PP	PPGSS	RKTLDN
CAP96550	Pe_chrys	HM	IMTS	PP	PPS	KDTLNN
CAK40369	As_niger	HM	IMTS	PP	PPG	KDTLNN
BAE61530	As_oryza	HM	MAQ	PP	PPYG	KDTLNN

		50	60	70	80
EHA51197	Ma_oryza	SKNNK	ITF	AGTA	VHGGGSCQVATY
EHA52406	Ma_oryza	STQK	LTF	QGGAT	HGGGSCQVALT
EHA52778	Ma_oryza	CAPIE	VQF	TGGAM	HGGGSCQFVAP
EAA35129	Ne_crass	DVQL	VQF	TGGAM	HGGGSCQFVSY
AE063862	Th_terre	GSQL	VNF	TGGAM	HGGGSCQFSLT
AE055680	My_therm	GSQV	VKF	TGGAM	HGGGSCQFSLT
EHA52554	Ma_oryza	SNQE	MVI	VGGAR	HNGGSCQASLS
AE063051	Th_terre	GTYN	FTV	AGGAP	HGGGSCQAAALS
CAP96976	Pe_chrys	SSQE	IQL	EGSAV	HGGGSCQALAL
CAK42338	As_niger	GTYE	LDL	QGSAT	HGGGSCQISLS
BAE59063	As_oryza	QEYE	IEL	QGSAT	HGGGSCQISLS
CBF89147	As_nidul	STYD	LEL	SGSAV	HGGGSCQIALS
CCD54857	Bo_fucke	QTAN	WTV	GTGAI	HGGGSCQVALS
EHA57166	Ma_oryza	QKSN	MTI	MGGAM	HNGGSCQASLS
EAA34256	Ne_crass	QTYN	MTT	AGTAT	HGGGSCQLSLS
AE061991	My_therm	SEYQ	FKMAA	GGARH	GGSQVSLS
CAP70884	Po_anser	GSYQ	PKV	TGGAP	HGGGSCQVSLS
AE071776	Th_terre	GTYN	FTV	VGGAP	HGGGSCQVSLS
CBX94475	Le_macul	BPQT	IKP	SGTA	VHGGGSCQISVT
EAA28891	Ne_crass	SKQP	LRL	IGTA	VHGGGSCQISIT
CBX92880	Le_macul	STQK	LAF	VGTAT	HGGGSCQVSVT
CCD52974	Bo_fucke	GSYD	LAF	KGSAT	HGGGSCQVSVT
CAP73493	Po_anser	STQI	MAF	TGSAT	HGGGSCQVSVT
CBF74037	As_nidul	QEHT	LEF	TGGAT	HGGGSCQISIT
CAP86617	Pe_chrys	SNNS	IKL	LGSAT	HGGGSCQVSLT
CAP79267	Pe_chrys	SNNS	IKL	LGSAT	HGGGSCQVSLT
CAP79288	Pe_chrys	SNNS	IKL	LGSAT	HGGGSCQVSLT
CAP96550	Pe_chrys	BSHP	LTF	VGSAT	HGGGSCQISLT
CAK40369	As_niger	BSMP	LTF	EGSAT	HGGGSCQVSLT
BAE61530	As_oryza	QSMP	LSP	IGSAT	HGGGSCQVSLT

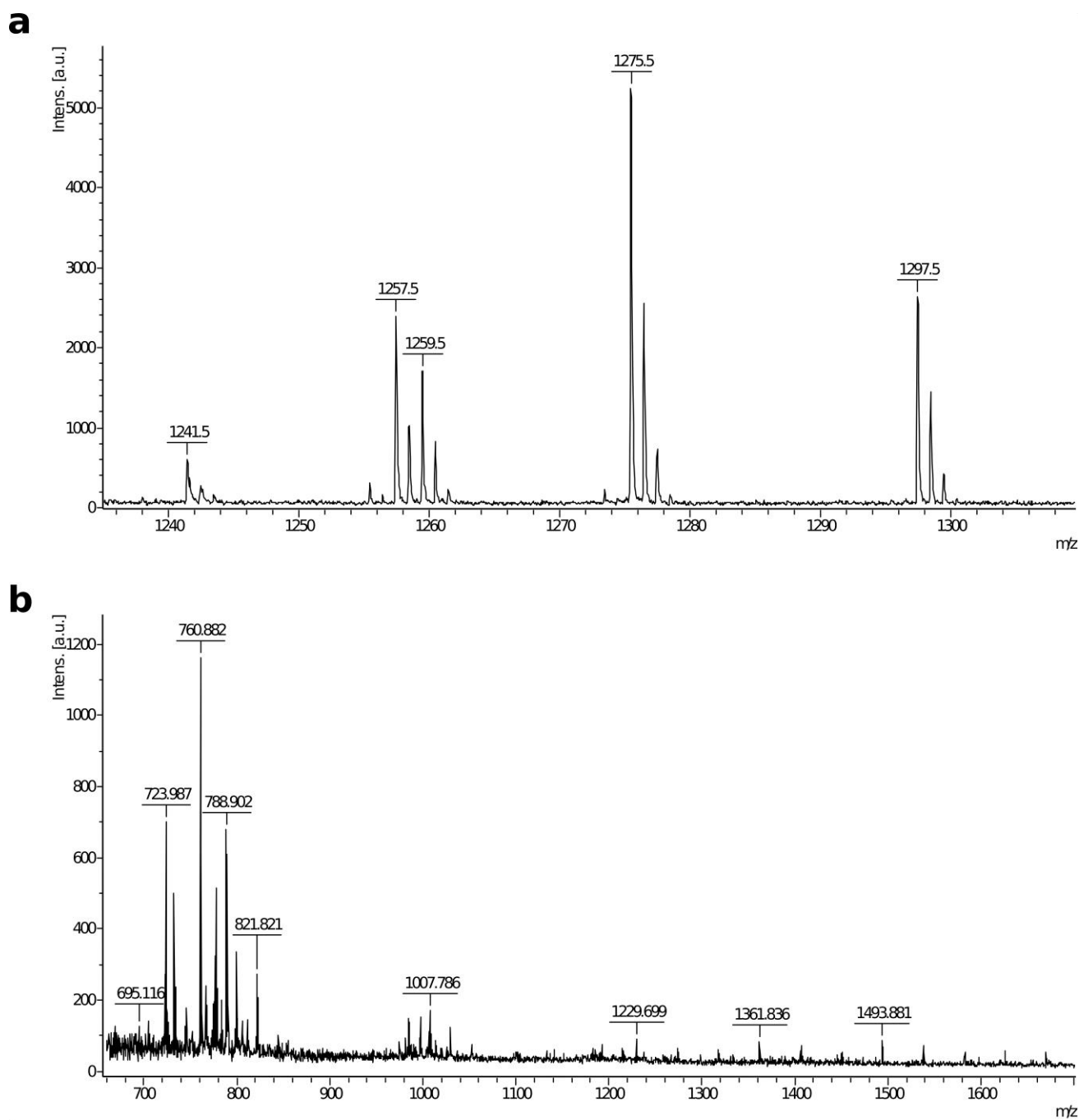
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EHA51197	Ma_oryza	PMENGN	ENLMPADA	AKPLDSGLT	YD	VP	EGIG	PGGN
EHA52406	Ma_oryza	PLSSD	GNL	GNDA	SALDSGLG	FK	IP	DDI
EHA52778	Ma_oryza	DPEGR	PTAQ	QCTSF	FEKEBCLK	TPK	IP	VP
EAA35129	Ne_crass	DAQQR	LNTDFC	NNDS	SGIDCT	REPL	IP	IP
AE063862	Th_terre	DEDEGR	ADSPHC	GNDS	GTBCIR	QFEP	IP	IP
AE055680	My_therm	DEDEGR	ADSPHC	GNDS	GTBCIR	QFEP	IP	IP
EHA52554	Ma_oryza	PPASQ	SALI	FKV	PSDAPS	GNVLF	AW	SW
AE063051	Th_terre	PGLSP	QSSP	GFV	PLPHDV	PATK	GA	V
CAP96976	Pe_chrys	PIDK	KYE	FEV	PSDAPS	GNVLF	AW	SW
CAK42338	As_niger	PLTE	SYK	FTI	PSDAP	TG	ALL	T
BAE59063	As_oryza	PIBK	KYK	FTI	PSDAP	TG	ALL	T
CBF89147	As_nidul	PITK	SYK	FTI	PSDAP	TG	ALL	T
CCD54857	Bo_fucke	PVAVD	SSAD	FTV	PSDAP	TG	ALL	T
EHA57166	Ma_oryza	PVSGG	SSFD	FTI	PSDAP	TG	ALL	T
EAA34256	Ne_crass	PLAG	KYD	FTI	PSDAP	TG	ALL	T
AE061991	My_therm	PLED	SYK	FTI	PSDAP	TG	ALL	T
CAP70884	Po_anser	PLAS	SYK	FTI	PSDAP	TG	ALL	T
AE071776	Th_terre	PLSS	NYD	FTI	PSDAP	TG	ALL	T
CBX94475	Le_macul	PQVD	GTTN	EYE	FTI	PSDAP	TG	ALL
EAA28891	Ne_crass	IARNE	GGNR	PGAS	AVQVNP	DSYE	YI	PD
CBX92880	Le_macul	VNSP	GNL	PEAG	SDSD	T	FP	VE
CCD52974	Bo_fucke	P.MKN	VAGNL	GNDA	NAID	PD	TYN	FT
CAP73493	Po_anser	PARNQ	AGN	ILPD	NAAL	BGV	VDN	YE
CBF74037	As_nidul	D.PNE	ANTNQ	GGD	AGM	KNG	FRPS	FP
CAP86617	Pe_chrys	PAKGP	GNL	DGSA	ESD	HSL	QLH	FA
CAP79267	Pe_chrys	PAKGP	GNL	DGSA	ESD	HSL	QLH	FA
CAP79288	Pe_chrys	PAKGP	GNL	DGSA	ESD	HSL	QLH	FA
CAP96550	Pe_chrys	PANVD	GNM	SGGP	DPD	PT	YD	FK
CAK40369	As_niger	PANVD	GNL	SGG	ASMA	DPT	KFN	YT
BAE61530	As_oryza	PANVD	GNL	SGG	PTST	G	KFT	YT

			160	170
EHA51197	Ma_oryza	.....	KAALBKIPSIATFNIPG.....	SG.CDT..
EHA52406	Ma_oryza	.....	KSNLDKLEIFVTNSPS.....	SNTCQT..
EHA52778	Ma_oryza	.....	AAGQSYLNSIPFVANI KGNP.....	VSTCTT..
EAA35129	Ne_crass	.....	PEKYESI PNIFIANI PKQKGIPGYDG.....	CVTGG
AE063862	Th_terre	.....	QSFFDALPEMFVANVPG.....	E..CTT..
AE055680	My_therm	.....	DKFLQELPDLFVANVDG.....	E..CTT..
EHA52554	Ma_oryza	.....	EPVAFNSRPPELLVNLGN.....	G..CTA..
AE063051	Th_terre	.....	GSEKVAFGSEFVIFKANVGN.....	G..CRT..
CAP96976	Pe_chrys	KEAPKPMLEKNTKKEHNNKSNQTPNNKPNSTHTNAKSSFDSTPDLFLANVDQ.....	AGKCVT..	
CAK42338	As_niger	LEB.....	MRKRDAFSSIPPIFLANVNG.....	PQCCTT..
BAE59063	As_oryza	TNA.....	LSRRDSFDSTPEIFQANNNG.....	PQCCTT..
CBF89147	As_nidul	FTA.....	VSKSQAFSSIPPLFLANVNG.....	PQCCTT..
CCD54857	Bo_fucke	.....	AAPAVAFSSRPDLFLVNLNN.....	G..CTS..
EHA57166	Ma_oryza	RGMQPQ.....	ARAAVPPAQRPAFLSNIGN.....	G..CKT..
EAA34256	Ne_crass	.....	DVAGAAFSTRPQIFVANVGN.....	G..CKT..
AE061991	My_therm	SKKREVA.....	ERADTAFSSRPVVFANIGN.....	G..CTT..
CAP70884	Po_anser	IEAPKVEQAQAVQ.....	KRASVGFSSRPALFVANIEN.....	G..CSV..
AE071776	Th_terre	ADEVEK.....	RASSTPFSQRPPVFANLNN.....	G..CTV..
CBX94475	Le_macul	.....	DSAFKQIPDMLKANLDQ.....	T..CKS..
EAA28891	Ne_crass	.....	KETFESI PDILVANLDN.....	G..CGT..
CBX92880	Le_macul	.....	TKEFDALPDMAVANINA.....	PGSCGKT..
CCD52974	Bo_fucke	DLI.....	ARDQAAFNALPDMPTANIDN.....	G..GST..
CAP73493	Po_anser	.....	EDALAAIPDMPTANIGG.....	D..CTTVG
CBF74037	As_nidul	SDV.....	AAVEKRAQSYPPMFIANING.....	.....CKT..
CAP86617	Pe_chrys	S.....	DNTPKQSLAPPPMFIANVNG.....	.....CIIT..
CAP79267	Pe_chrys	S.....	DNKPKQSLAPPIFIANVNG.....	.....CIIT..
CAP79288	Pe_chrys	S.....	DNTPKQSLAPPPMFIANVNG.....	.....CIIT..
CAP96550	Pe_chrys	P.....	EELEKRSSSPPPMFVANVNG.....	.....CTT..
CAK40369	As_niger	DVEBEK.....	RDVEKRSSSPPPMFVANVNG.....	.....CTT..
BAE61530	As_oryza	EVPKE.....	KTVEKRSSSPPPMFVANVNG.....	.....CTT..

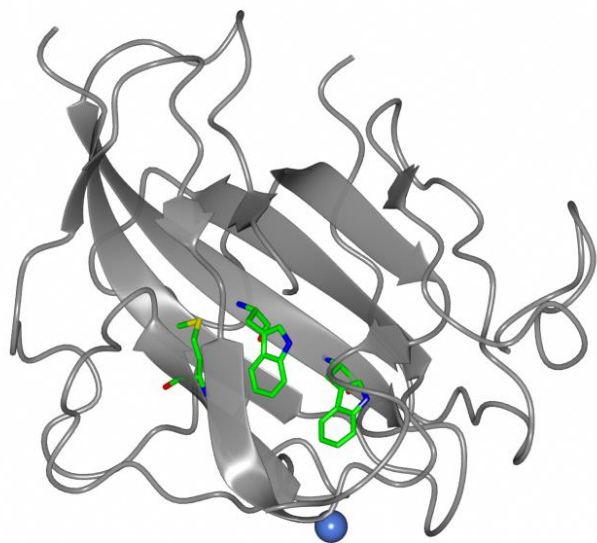
  

		180	190	200
EHA51197	Ma_oryza	QAQDFSYEFEGPVVRIGHS.....	RPMKVLKG	C
EHA52406	Ma_oryza	PEGSDYAYENPGAVVFNKGN.....	PSRLVKLT	C
EHA52778	Ma_oryza	SPGV.LGFFEGSVGMVLQP.....	PTAGSSGS	C
EAA35129	Ne_crass	GAANVVNIENPGKYGRIINQLKRPFPSKPDPAPTGLNL	C	C
AE063862	Th_terre	GNGV.LNIENPGNYGRLLAQ.....	PTDGSNGN	C
AE055680	My_therm	GNGV.FNIENPGKYGVLED.....	PTQGSSEGS	C
EHA52554	Ma_oryza	KEGIDVDPEFPGPVSRAGN.....	SAAPPSPGN	C
AE063051	Th_terre	VD.SANVKFDEGPDVDANG.....	PATPPTGS	C
CAP96976	Pe_chrys	IEGEPVHFKEGPKLIG.....	KAEGPGYK	C
CAK42338	As_niger	IEINYDVNFELPGPSVEGSI.....	NGTDAGFT	C
BAE59063	As_oryza	TEGEEVNFELPGPSKEG.....	SLSGKGYT	C
CBF89147	As_nidul	IEGEEVNFEMPGPSVEG.....	SLSGTGYK	C
CCD54857	Bo_fucke	VENKAVNYENPGPDADVTRKTS.....	DSGTFTGT	C
EHA57166	Ma_oryza	.ENMVVDYENPGPDVIR.....	KGTATKPS	C
EAA34256	Ne_crass	DENFVDQYQEPGNVVKASDA.....	PVKGPEGS	C
AE061991	My_therm	VEGVDVDYQEPGPDVVRSGD.....	KIGPPSPGN	C
CAP70884	Po_anser	AE GTDVVYENPGPDVINNGG.....	STGAPSPGN	C
AE071776	Th_terre	AE GVDVEYENPGPDVVKSGS.....	RLGPPQGN	C
CBX94475	Le_macul	EANFAVSYFSEGTAVQKGSTND.....	AKPPVGEA	C
EAA28891	Ne_crass	PENKDILFENPGQNVKANGATDA.....	FAAPTQQG	C
CBX92880	Le_macul	PEGFDYTFANPGNYVTKGS.....	SAFKPL	C
CCD52974	Bo_fucke	KDSTDLVPEFGDSVDYDEGSTT.....	ATAGPTGS	C
CAP73493	Po_anser	ADSKDILFENPGSSVETNGDVS.....	AMVPPTGN	C
CBF74037	As_nidul	EQNMSPRYFENPGSMVETLNEAH.....	LIPDANNV	C
CAP86617	Pe_chrys	RENVDIHFEPFGSIVEYNGDSKY.....	RPQEGEPV	C
CAP79267	Pe_chrys	RENVDIHFEPFGSIVEYNGDSKY.....	RPQEGEPV	C
CAP79288	Pe_chrys	RENVDIHFEPFGSIVEYNGDSKY.....	RPQEGEPV	C
CAP96550	Pe_chrys	KE SVDIRFQAGDNVEYKQGPNG.....	LAAEGSEA	C
CAK40369	As_niger	SE GVDIRFQEGDDIQYNGEPSN.....	LASAGAAA	C
BAE61530	As_oryza	KE GVDIRFENPGSIVEYAGDKSN.....	LAAEGSQA	C

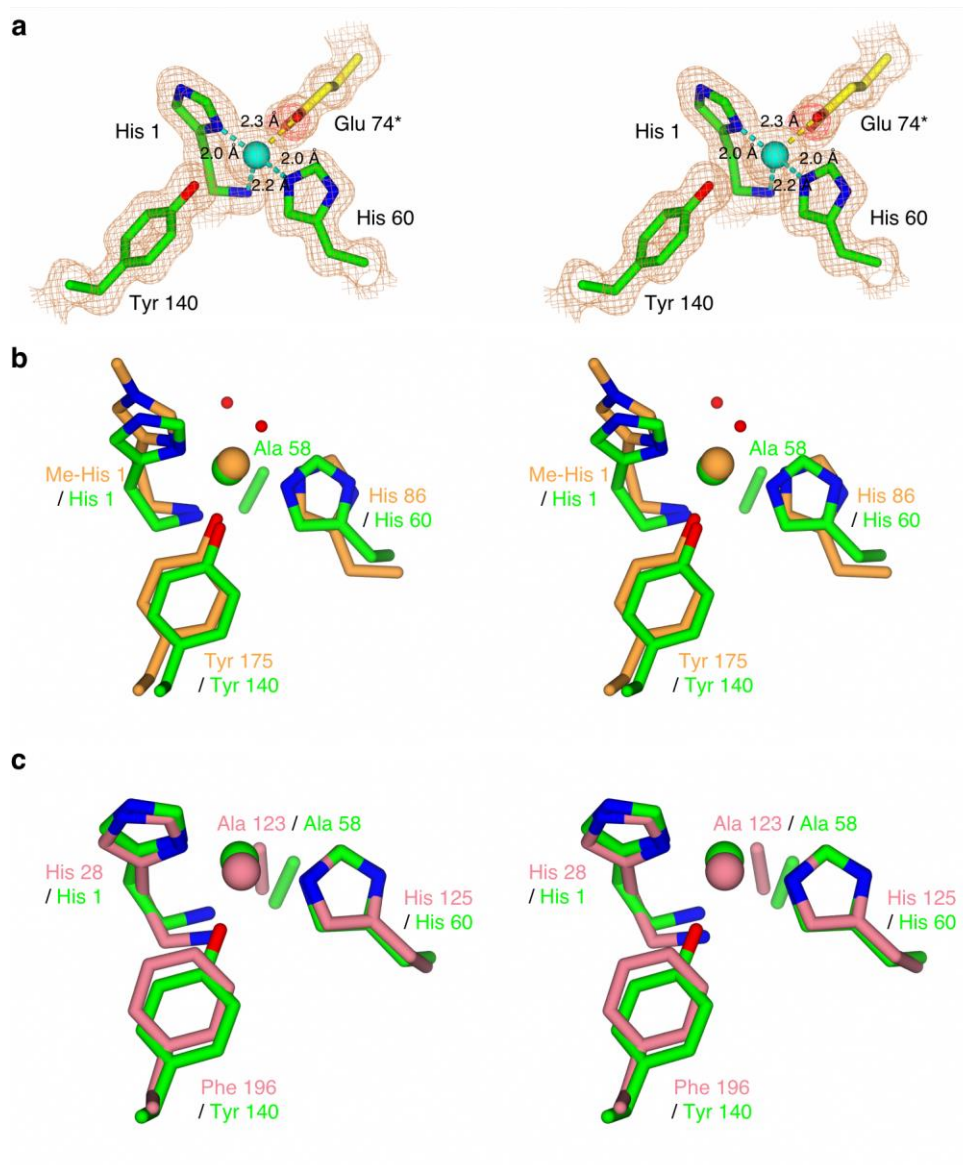
Supplementary Figure 2 AA11 partial alignment



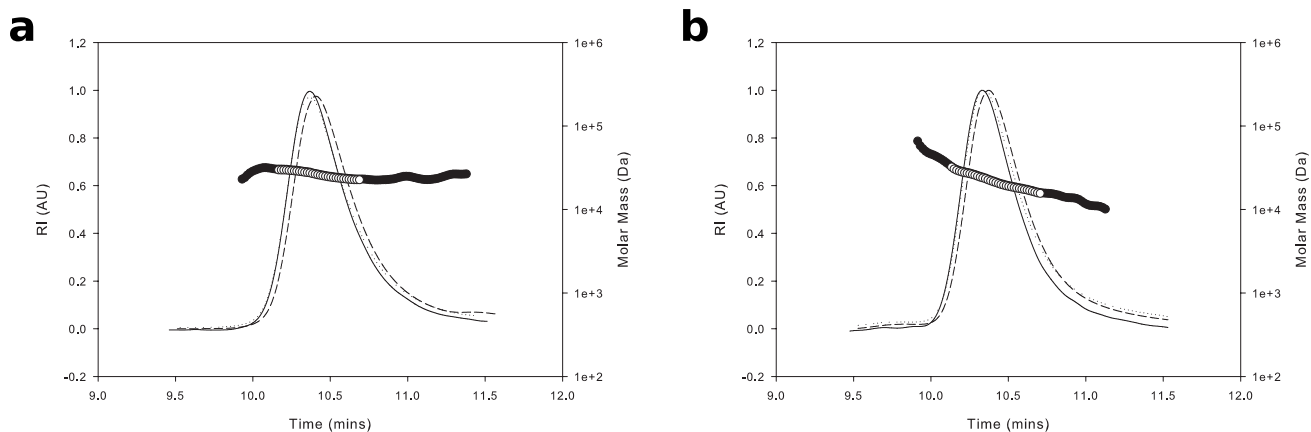
Supplementary Figure 3. MALDI-TOF analysis of a) *Ao*(AA11) action (in presence of ascorbate) on squid-pen chitin, blow-up of DP6 region, b) same conditions but no *Ao*(AA11)



Supplementary Figure 4. Ribbon depiction of Cu-Ao(AA11) with conserved tryptophan residues highlighted as sticks.



Supplementary Figure 5. Stereo views of (a) the electron density maps contoured at  $1\sigma$  in the active site of Cu-Ao(AA11), (b) Stereo view of the active site overlay of Ao(AA11) (green carbons/copper) with Cu-AA9 from *T. aurantiacus*, and (c) the active site overlap of Cu-Ao(AA11) (green carbons/copper) with Cu-(AA10) from *B. amyloliquefaciens* (pink carbons/copper). See legend to Figure 4 for further details.



Supplementary Figure 6. SEC-MALLS Data for (A) Ao(AA11) in the presence of EDTA and (B) Ao(AA11) in the presence of Cu<sup>2+</sup>. The Rayleigh ratio, UV light absorbance and differential refractive index of the solution emerging from the size exclusion column are represented by solid, dashed and dotted lines respectively. The molecular mass calculated from the MALLS data across the selected peak is shown by open and closed circles giving values of  $26.3 \pm 3.2$  kDa and  $22.0 \pm 2.4$  kDa in the presence of EDTA and Cu<sup>2+</sup> respectively indicating the protein is monomeric in both cases.

Supplementary Table 1. Data collection, phasing and refinement statistics

	Zn <sup>2+</sup> SAD (4MAH)	Cu(I) (4MAI)
<b>Data collection</b>		
Space group	P2 <sub>1</sub> 2 <sub>1</sub> 2 <sub>1</sub>	P2 <sub>1</sub> 2 <sub>1</sub> 2 <sub>1</sub>
Cell dimensions		
$a, b, c$ (Å)	55.2, 61.5, 65.1	56.3, 60.6, 65.2
$\alpha, \beta, \gamma$ (°)	90.0, 90.0, 90.0	90.0, 90.0, 90.0
Wavelength (Å)	1.282	0.980
Resolution (Å)	28.05–1.55 (1.58–1.55)	44.39–1.40 (1.42–1.40)
$R_{\text{merge}}$	0.05 (0.37)	0.05 (0.74)
$I / \sigma I$	16.4 (3.6)	17.9 (2.0)
Completeness (%)	98.7 (94.2)	99.3 (95.7)
Redundancy	5.4 (4.0)	6.3 (5.1)
<b>Refinement</b>		
Resolution (Å)	28.07 – 1.55	42.63 – 1.40
No. reflections (Work/Free)	30,691/1619	42,001/2200
$R_{\text{work}} / R_{\text{free}}$	0.13/0.17	0.13/0.15
No. atoms		
Protein	1,383	1,381
Ligand/ion	6	14
Water	147	187
<i>B</i> -factors		
Protein	19	17
Ligand/ion	34	35
Water	30	32
R.m.s deviations		
Bond lengths (Å)	0.010	0.009
Bond angles (°)	1.42	1.42

\*A single crystal was used for both structures. \*Values in parentheses are for highest-resolution shell.



Supplementary Table 2. EPR spin Hamiltonian parameters for Cu-Ao(AA11)

Sample	$g_x$	$g_y$	$g_z$	$A_x$ /G	$A_y$ /G	$A_z$ /G	Strains
Cu-Ao(AA11) pH 5	2.034	2.10	2.275	12	17	157	A/G 20, 110, 0  $g$ 0.02, 0.025, 0.02
Cu-Ao(AA11) pH 5 + excess azide	2.06	2.06	2.24	20	20	175	A/G 10, 90, 0  $g$ 0.04, 0.06, 0.02

Supplementary Table 3. Known spin Hamiltonian parameters for LPMOs with CAZy classification

CAZy classification (substrate)	$g_x$	$g_y$	$g_z$	$A_z$ /G	Deviation from axial type 2	Source
<i>met</i> -Cu-AA9 <i>T. aurantiacus</i> (cellulose)	2.06	2.06	2.27	153	None	Ref 4
<i>met</i> -Cu-AA10 <i>B. amyloliquefaciens</i> (chitin)	2.05	2.08	2.23	125	reduced $A_z$ value some rhombicity in $g_{x,y}$	Ref 14
<i>met</i> -Cu-AA11 <i>A. oryzae</i> (chitin)	2.04	2.10	2.28	157	rhombicity in $g_{x,y}$	this work

## REFERENCES

1. Hemsworth, G.R. et al. The copper active site of CBM33 polysaccharide oxygenases. *Journal of the American Chemical Society* **135**, 6069-77 (2013).